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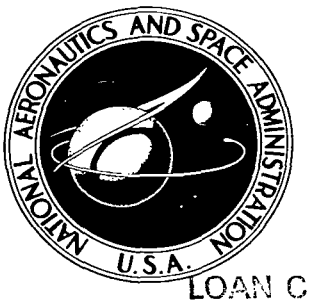

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LOW-COVERAGE HEAT OF ADSORPTION

II — ALKALI METAL ATOMS ON TUNGSTEN; LENNARD-JONES ATOM-ATOM INTERACTION THEORY

by Harold E. Neustadter, Keung P. Luke, and Thomas Sheahan

Lewis Research Center
Cleveland, Ohio

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SUMMARY

A comparison of experimental values of heat of adsorption (in the limit of zero coverage) for sodium, rubidium, and cesium on a tungsten substrate is made with those calculated from an adaptation of the Lennard-Jones atom-atom interaction potential to adsorption. A new method is presented for performing the necessary summations for three specific sites on the (100) and (110) planes, and comparisons are made with existing approximation methods.

INTRODUCTION

Considerable interest in alkali metal plasma for power generation and space propulsion has prompted extensive studies of adsorption of alkali metals on various substrates. A requirement for an adequate theory is the specification of the heat of adsorption in the limit of zero coverage. This report compares experimental values of heat of adsorption for sodium, rubidium, and cesium on a tungsten substrate in the limit of zero coverage (table I) to calculations made with the application of the Lennard-Jones interaction-potential function. The potential function parameters are evaluated, and results are indicated.

TABLE I. - EXPERIMENTAL ZERO-COVERAGE HEATS OF ADSORPTION

Source	Sodium	Rubidium	Cesium
	Heat of adsorption, φ, ev		
Bosworth (ref. 1)	-1.38		
Hughes (ref. 2)		-2.6	
de Boer and Veenemans (ref. 3)			-3.0
Taylor and Langmuir (ref. 4)			-2.79
Becker (ref. 5)			-2.40

ATOM-ATOM INTERACTIONS

The use of an interatom potential is based on (1) establishing the relation governing the interaction between one alkali atom and one tungsten atom and (2) summing this interaction over all atoms in the tungsten substrate. This assumes additivity of the separate interactions and neglects any effect one tungsten atom might have

on another because of the presence of the adsorbate. While the second assumption apparently neglects the metallic nature of the substrate, this model nevertheless is applicable to adsorption on a metal at high temperatures (refs. 6 and 7).

There have been many interaction potentials proposed (ref. 8). Of particular interest is the Lennard-Jones 6-12 potential

$$E_{L\text{-}J}(r) = 4\epsilon_{12}\left[\left(\frac{\sigma_{12}}{r}\right)^{12} - \left(\frac{\sigma_{12}}{r}\right)^{6}\right] \tag{1}$$

where ϵ_{12} is the energy at equilibrium, and σ_{12} is (to a close approximation) the distance of closest approach of the two atoms.[1] (Symbols are defined in appendix A.)

The interaction energy between one adsorbed atom and the entire metal substrate is obtained by summing equation (1) over all the atoms in the metal:

$$\varphi(r_i) = \sum_{i=1}^{\infty} E_{L\text{-}J}(r_i) = 4\epsilon_{12}\sum_{i=1}^{\infty}\left[\left(\frac{\sigma_{12}}{r_i}\right)^{12} - \left(\frac{\sigma_{12}}{r_i}\right)^{6}\right] \tag{2}$$

The authors of this report have been able to express this sum in a form that permits its rigorous calculation as a function of the distance z from the plane through the centers of the atoms of the outermost layer of substrate to the center of the adsorbed atom. The use of the Lennard-Jones potential in this manner has the distinct advantage over previous works (ref. 9) of distiguishing between any two adsorption sites and between any two exposed substrate surfaces. Equation (2) can be rewritten as

$$\varphi(r_i) = 4\epsilon_{12}S_{12\text{-}6} \tag{3}$$

The heat of adsorption φ is the bond energy of the adsorbed atom when the system is in equilibrium. Therefore, φ is the minimum value of $\varphi(r_i)$ considered as a function of z. Or,

$$\varphi = 4\epsilon_{12}(S_{12\text{-}6})_{min} \tag{4}$$

---

[1] Another interatom potential is the angle-independent Stockmeyer potential (ref. 3) for identical parallel polar molecules:

$$\Phi(r) = 4\epsilon_{12}\left[\left(\frac{\sigma_{12}}{r}\right)^{12} - \left(\frac{\sigma_{12}}{r}\right)^{6}\right] + \frac{m_o^2}{r^3 + \alpha} \tag{1a}$$

where m_o is the molecule dipole moment, and α is its polarizability. This would be of interest in an extension of the method of this section to include the effects of the interaction of neighboring adsorbed particles.

where $(S_{12-6})_{min}$ is S_{12-6} at that value of z for which $\partial(S_{12-6})/\partial z = 0$.

CALCULATIONS

The usual combining rule (ref. 8) gives σ_{12} as

$$\sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22}) \tag{5}$$

while ϵ_{12} is evaluated (see appendix B) from a comparison of the attractive term in equation (1) with the dispersion force derived by Kirkwood (ref. 10) and Muller (ref. 11) to give

$$4\epsilon_{12}(\sigma_{12})^6 = \frac{6\mu c^2 \alpha_M \alpha_A}{\frac{\alpha_A}{\chi_A} + \frac{\alpha_M}{\chi_M}} \tag{6}$$

Substitution of numerical values results in

$$\varphi = \frac{0.093\,\alpha_A}{1.957\left(\frac{\alpha_A}{n_A}\right)^{1/2} + 0.393} \frac{(S_{12-6})_{min}}{(\sigma_{12})^6} \tag{7}$$

The details of the summation technique employed in evaluating S_{12-6} are given in appendix C.[2] The evaluations of S_{12-6} and $(S_{12-6})_{min}$ were performed for three sites (A, B, and C of fig. 1) on both the (100) and (110) planes. The results are shown in tables II and III. Because the process of preparing and aging tungsten emitters transforms the exposed surface into essentially a (110) plane (refs. 4, 5, and 12), the calculations involving equation (7) were done for the (110) plane only. Similarly, only the model of an atom in the center of the unit cell, the location that corresponds to the site of the strongest bond (site A of fig. 1(b)), was used in the present calculation of φ. That site

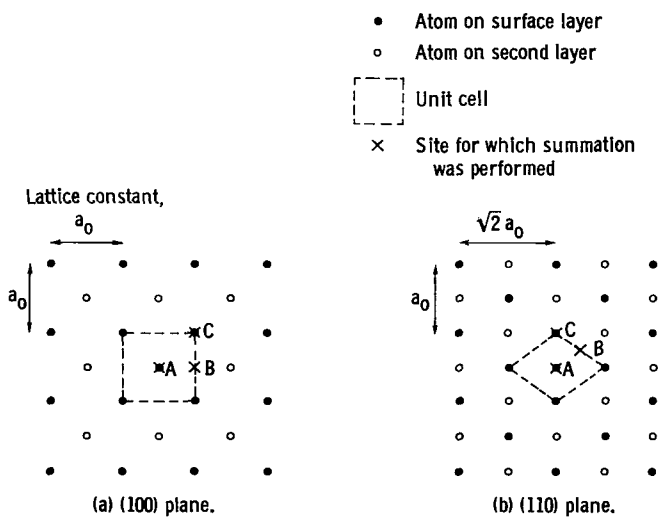

Figure 1. - (100) and (110) planes of body-centered cubic metal with lattice constant a_0. (See appendix C.)

[2]Care was taken to perform the summations in a general form to make the results applicable to any body-centered cubic substrate.

TABLE II. - VALUES FOR EQUATIONS (C1) and (C2)

[E-01, E-02, E-03, etc., denote exponents 10^{-1}, 10^{-2}, 10^{-3}, etc., respectively; E 01, E 02, E 03, etc., denote exponents of 10^{1}, 10^{2}, 10^{3}, etc., respectively.]

(a) (100) plane

l	Site A		Site B		Site C	
	S_6	S_{12}	S_6	S_{12}	S_6	S_{12}
1	0.8691E 00	0.1678E-00	0.1995E 01	0.1590E 01	----------	----------
2	.5801E 00	.5714E-01	.1426E 01	.8241E 00	----------	----------
3	.4044E-00	.2677E-01	.8967E 00	.3172E-00	0.2155E 02	0.4593E 03
4	.2795E-00	.1271E-01	.5275E 00	.1032E-00	.3905E 01	.1455E 02
5	.1904E-00	.5755E-02	.3055E-00	.3147E-01	.1069E 01	.1000E 01
6	.1289E-00	.2506E-02	.1800E-00	.9592E-02	.3886E-00	.1123E-00
7	.8764E-01	.1073E-02	.1098E-00	.3035E-02	.1741E-00	.1775E-01
8	.6031E-01	.4609E-03	.6993E-01	.1016E-02	.9150E-01	.3615E-02
9	.4226E-01	.2011E-03	.4642E-01	.3634E-03	.5414E-01	.8992E-03
10	.3023E-01	.8992E-04	.3204E-01	.1389E-03	.3495E-01	.2634E-03
11	.2210E-01	.4143E-04	.2290E-01	.5677E-04	.2404E-01	.8857E-04
12	.1651E-01	.1973E-04	.1687E-01	.2468E-04	.1733E-01	.3346E-04
13	.1259E-01	.9723E-05	.1275E-01	.1137E-04	.1294E-01	.1395E-04
14	.9788E-02	.4958E-05	.9861E-02	.5523E-05	.9941E-02	.6328E-05
15	.7738E-02	.2615E-05	.7772E-02	.2813E-05	.7806E-02	.3075E-05
16	.6213E-02	.1424E-05	.6230E-02	.1496E-05	.6244E-02	.1584E-05
17	.5059E-02	.8004E-06	.5067E-02	.8267E-06	.5073E-02	.8578E-06
18	.4170E-02	.4629E-06	.4175E-02	.4728E-06	.4177E-02	.4841E-06
19	.3476E-02	.2751E-06	.3479E-02	.2789E-06	.3479E-02	.2831E-06
20	.2927E-02	.1677E-06	.2929E-02	.1692E-06	.2929E-02	.1708E-06
21	.2487E-02	.1047E-06	.2488E-02	.1052E-06	.2488E-02	.1059E-06
22	.2130E-02	.6679E-07	.2131E-02	.6702E-07	.2131E-02	.6726E-07
23	.1838E-02	.4346E-07	.1839E-02	.4356E-07	.1839E-02	.4365E-07
24	.1597E-02	.2882E-07	.1598E-02	.2885E-07	.1597E-02	.2889E-07
25	.1396E-02	.1944E-07	.1397E-02	.1945E-07	.1396E-02	.1947E-07
26	.1227E-02	.1332E-07	.1228E-02	.1332E-07	.1228E-02	.1333E-07
27	.1085E-02	.9266E-08	.1085E-02	.9269E-08	.1085E-02	.9272E-08
28	.9636E-03	.6533E-08	.9641E-03	.6534E-08	.9636E-03	.6535E-08
29	.8595E-03	.4665E-08	.8600E-03	.4666E-08	.8595E-03	.4666E-08
30	---------	---------	.7702E-03	.3371E-08	.7698E-03	.3372E-08

A corresponds to the strongest bond can be seen from figure 2, in which, for a given value of σ_{12}/a_o (for a given physical system), position A yields the lowest (largest absolute) value for $(S_{12-6})_{min}$.

The results of this summation method are compared with those of two approximate methods in appendix D. Both approximation techniques have the drawback of being unable to distinguish between different adsorption sites.

Although α_A must be known to use equation (7), there are no uniquely determined values for the polarizability (see table IV). Therefore, the application of equation (7) necessarily reduces to a parametric study of φ as a function of α. The results (table V) show that reasonable values of φ are obtained from equation (6) when the experimental values of α are used.

TABLE II. - Concluded. VALUES FOR EQUATIONS (C1) and (C2)

[E-01, E-02, E-03, etc., denote exponents 10^{-1}, 10^{-2}, 10^{-3}, etc., respectively; E 01, E 02, E 03, etc., denote exponents of 10^{1}, 10^{2}, 10^{3}, etc., respectively.]

(b) (110) plane

l	Site A		Site B		Site C	
	S_6	S_{12}	S_6	S_{12}	S_6	S_{12}
1	0.2144E 01	0.1611E 01	0.4273E 01	0.8233E 01	----------	----------
2	.1569E 01	.8415E 00	.2827E 01	.3525E 01	----------	----------
3	.1013E 01	.3279E-00	.1599E 01	.1071E 01	0.2161E 02	0.4593E 03
4	.6134E 00	.1088E-00	.8517E 00	.2787E-00	.3954E 01	.1455E 02
5	.3653E-00	.3407E-01	.4554E-00	.7045E-01	.1106E 01	.1001E 01
6	.2201E-00	.1072E-01	.2530E-00	.1856E-01	.4161E-00	.1127E-00
7	.1357E-00	.3519E-02	.1481E-00	.5271E-02	.1933E-00	.1796E-01
8	.8695E-01	.1221E-02	.9152E-01	.1633E-02	.1054E-00	.3719E-02
9	.5796E-01	.4511E-03	.5941E-01	.5532E-03	.6357E-01	.9498E-03
10	.3963E-01	.1773E-03	.4030E-01	.2038E-03	.4161E-01	.2881E-03
11	.2817E-01	.7397E-04	.2838E-01	.8120E-04	.2900E-01	.1007E-03
12	.2071E-01	.3264E-04	.2064E-01	.3469E-04	.2066E-01	.3955E-04
13	.1543E-01	.1518E-04	.1543E-01	.1578E-04	.1555E-01	.1706E-04
14	.1177E-01	.7408E-05	.1181E-01	.7590E-05	.1177E-01	.7943E-05
15	.9306E-02	.3779E-05	.9227E-02	.3835E-05	.9239E-02	.3937E-05
16	.7354E-02	.2006E-05	.7334E-02	.2024E-05	.7291E-02	.2054E-05
17	.5986E-02	.1106E-05	.5919E-02	.1111E-05	.5832E-02	.1120E-05
18	.4923E-02	.6301E-06	.4841E-02	.6316E-06	.4843E-02	.6345E-06
19	.4023E-02	.3696E-06	.4008E-02	.3703E-06	.3984E-02	.3709E-06
20	.3398E-02	.2233E-06	.3353E-02	.2232E-06	.3352E-02	.2236E-06
21	.2888E-02	.1382E-06	.2832E-02	.1381E-06	.2793E-02	.1380E-06
22	.2404E-02	.8735E-07	.2413E-02	.8740E-07	.2392E-02	.8731E-07
23	.2103E-02	.5657E-07	.2072E-02	.5648E-07	.2069E-02	.5649E-07
24	.1800E-02	.3721E-07	.1792E-02	.3721E-07	.1765E-02	.3714E-07
25	.1555E-02	.2494E-07	.1560E-02	.2495E-07	.1576E-02	.2496E-07
26	.1391E-02	.1704E-07	.1365E-02	.1700E-07	.1363E-02	.1700E-07
27	.1206E-02	.1176E-07	.1202E-02	.1176E-07	.1183E-02	.1173E-07
28	.1060E-02	.8249E-08	.1063E-02	.8253E-08	.1076E-02	.8258E-08
29	.9650E-03	.5884E-08	.9456E-03	.5865E-08	.9234E-03	.5842E-08
30	---------	---------	.8442E-03	.4218E-08	.8294E-03	.4201E-08

CONCLUDING REMARKS

The Lennard-Jones interatom potential can be used in conjunction with a physical model based on a discrete adsorption site on the (110) plane of a perfect crystal to obtain values of φ in agreement with experimental values. The particular advantages of this approach lie in its ability to distinguish between any two adsorption sites and between any two exposed substrate surfaces. Because of this unique feature it can be shown that the intuitive adsorption site corresponding to the location of an atom in the center of the unit cell (site A of fig. 1(b)) is actually the position of the strongest adsorption bond.

Unfortunately, the experimental values of φ had to be collected from a

TABLE III. - LENNARD-JONES INTERACTION ENERGY SUMMATION AND NORMALIZED EQUILIBRIUM DISTANCE FOR ADSORPTION ON BODY-CENTERED CUBIC SUBSTRATE

(a) (100) plane

Reduced Lennard-Jones parameter, σ_{12}/a_o	Site A		Site B		Site C	
	$(S_{12-6})_{min}$	l_{min}	$(S_{12-6})_{min}$	l_{min}	$(S_{12-6})_{min}$	l_{min}
0.600	0.880	4.257	0.733	5.065	0.429	6.746
.642	.954	4.912	.789	5.639	.513	7.145
.683	1.032	5.509	.871	6.166	.566	7.506
.725	1.121	6.068	.944	6.693	.659	7.935
.767	1.204	6.620	1.046	7.176	.771	8.267
.808	1.309	7.149	1.139	7.666	.853	8.675
.850	1.411	7.687	1.262	8.126	.982	9.055
.892	1.545	8.181	1.379	8.581	1.125	9.380
.933	1.680	8.644	1.523	9.032	1.250	9.835
.975	1.826	9.093	1.665	9.455	1.429	10.18
1.017	1.964	9.559	1.832	9.903	1.611	10.50
1.058	2.130	10.03	2.014	10.30	1.802	10.82
1.100	2.300	10.51	2.193	10.74	2.003	11.15
1.142	2.508	10.98	2.399	11.15	2.171	11.57
1.183	2.734	11.39	2.608	11.56	2.410	12.02
1.225	2.964	11.79	2.844	11.97	2.677	12.37
1.267	3.206	12.18	3.089	12.36	2.958	12.66
1.308	3.451	12.57	3.342	12.78	3.235	12.97
1.350	3.699	12.97	3.621	13.17	3.509	13.30
1.392	3.965	13.40	3.908	13.57	3.773	13.78
1.433	4.254	14.00	4.222	13.97	4.103	14.18
1.475	4.611	14.40	4.550	14.35	4.453	14.54
1.517	4.995	14.68	4.881	14.75	4.811	14.87
1.558	5.355	15.10	5.243	15.14	5.181	15.20
1.600	5.701	15.37	5.613	15.52	5.568	15.50

variety of experimental techniques and laboratory conditions of numerous workers. It must also be recognized that except for cesium adsorption there is only one reported value for each system. The results of this study must necessarily be considered within the framework of these limitations.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, June 1, 1964

TABLE III. - Concluded. LENNARD-JONES INTERACTION ENERGY SUMMATION AND NORMALIZED EQUILIBRIUM DISTANCE FOR ADSORPTION ON BODY-CENTERED CUBIC SUBSTRATE

(b) (110) plane

Reduced Lennard-Jones parameter, σ_{12}/a_o	Site A		Site B		Site C	
	$(S_{12-6})_{min}$	l_{min}	$(S_{12-6})_{min}$	l_{min}	$(S_{12-6})_{min}$	l_{min}
0.600	1.273	1.557	0.6891	4.374	0.3693	6.791
.642	1.451	2.039	.7368	5.031	.4346	7.184
.683	1.517	2.699	.7888	5.648	.4656	7.590
.725	1.531	3.579	.8572	6.211	.5386	8.022
.767	1.551	4.491	.9267	6.767	.6257	8.351
.808	1.590	5.306	1.016	7.270	.6864	8.807
.850	1.652	6.029	.105	7.786	.7908	9.170
.891	1.728	6.702	.217	8.252	.8841	9.541
.933	1.819	7.328	.328	8.736	1.007	9.933
.975	1.924	7.925	.463	9.182	1.146	10.26
1.017	2.040	8.490	1.599	9.633	1.280	10.64
1.058	2.174	9.037	1.759	10.06	1.445	11.00
1.100	2.317	9.563	1.922	10.48	1.627	11.33
1.142	2.480	10.07	2.107	10.91	1.802	11.70
1.183	2.651	10.56	2.308	11.31	2.011	12.05
1.225	2.844	11.05	2.511	11.74	2.233	12.37
1.267	3.046	11.52	2.740	12.13	2.462	12.74
1.308	3.269	11.98	2.975	12.53	2.719	13.09
1.350	3.508	12.42	3.233	12.93	2.991	13.41
1.392	3.757	12.88	3.509	13.32	3.267	12.78
1.433	4.032	13.31	3.792	13.72	3.574	14.12
1.475	4.315	13.74	4.100	14.10	3.888	14.46
1.517	4.625	14.16	4.420	14.48	4.225	14.82
1.558	4.945	14.58	4.765	14.87	4.580	15.16
1.600	5.293	14.99	5.132	15.24	4.947	15.51

TABLE IV. - ELECTRONIC POLARIZABILITY

Source	Sodium	Rubidium	Cesium
	Electronic polarizability, α, A^3		
Salop, Pollack, and Bedesson (ref. 13)	20±2.5	40±5	52.5±6.5
Chamberlain and Zorn (refs. 14 and 15)	21.5±2	38±4	48±6
Sternheimer (ref. 16)	22.9	49.1	67.7

TABLE V. - CALCULATIONS FROM EQUATION (6)[a]

Adsorbed atom	Equation from which interaction ϵ_{12} energy is evaluated	Reduced Lennard-Jones parameter, σ_{12}/a_o	Heat of adsorption, φ, ev (b)	Electronic polarizability, α, A^3	
				Calculated	From literature (c)
Sodium	(B1)	0.935	-1.38	37	17.5 to 23
	(B2)			48	
	(B3)			16	
Rubidium	(B1)	1.071	-2.6	144	34 to 50
	(B2)			>150	
	(B3)			54	
Cesium	(B1)	1.112	-2.4	165	42 to 68
			-3.0	210	
	(B2)	1.112	-2.4	>200	
			-3.0	>200	
	(B3)	1.112	-2.4	50	
			-3.0	66	

[a]Eq. (6) is eq. (4) with $4\epsilon_{12}(\sigma_{12})^6$ evaluated from eq. (B3).

[b]See table I.

[c]See table IV.

APPENDIX A

SYMBOLS

A,B,C	adsorption sites of fig. 1
a_o	lattice constant
C_6	defined by eq. (B4)
c	speed of light
d	distance between planes in substrate material
E	atom-atom attractive interaction energy
E_{L-J}	Lennard-Jones interaction potential function
e	electron charge
(hkl)	Miller indices, e.g., (100), (110)
$\hbar$	Plank's constant divided by 2π
I	ionization potential
l	defined by eq. (C3)
l_{min}	defined by eq. (C14)
m,n,p	dummy indices
m_o	molecule dipole moment
N	atomic volume density
n	number of electrons in atom
P	specific adsorption site, e.g., site A, B, or C of fig. 1
R	distance from metal surface to nucleus of adsorbed atom
r	interatom distance
r_i	distance from adsorbed atom to i^{th} substrate atom
S_6	defined by eq. (C1)
S_{12}	defined by eq. (C2)

S_{12-6}	defined by eq. (C13)
$(S_{12-6})_{min}$	defined by eq. (C15)
z	normal distance from substrate to adsorbed atom
α	electronic polarizability
ϵ_{12}	total interaction energy between atoms 1 and 2 at equilibrium
$\lambda_0, \lambda_1, \lambda_2$	defined by eqs. (C7), (C9), and (C11), respectively
μ	electron rest mass
σ	atomic surface density
σ_{12}	Lennard-Jones parameter of eq. (1) related to sizes of atoms 1 and 2
$\Phi(r)$	defined by eq. (1a)
φ	heat of adsorption in limit of zero coverage
$\varphi(r_i)$	energy of interaction between atom and metal as function of distance between them
χ	diamagnetic susceptibility
$\psi^{(3)}(\chi)$	third derivative of the Reimann-Zeta function

Subscripts:

A	adsorbed atom
M	substrate metal
min	minimum

APPENDIX B

EVALUATION OF TOTAL INTERACTION ENERGY BETWEEN TWO ATOMS

The forces between atoms can be divided into attractive and repulsive components. The attractive force is long range and arises from the interaction of the instantaneous distributions of the charges of the two neutral atoms (ref. 8). It is derivable from an interaction potential by expanding the charge distribution of each neutral atom in a multipole expansion and retaining only the leading, or dipole-dipole, term. This potential is then used in a quantum-mechanical variation procedure to obtain an expression for energy. London (ref. 17) derived such an expression,

$$E = - \frac{3\alpha_A\alpha_M}{2r^6} \frac{I_A I_M}{I_A + I_M} \tag{B1}$$

His result was followed by those of Slater and Kirkwood (ref. 18),

$$E = - \frac{3e\hbar}{2\sqrt{\mu}r^6} \frac{\alpha_A\alpha_M}{\left(\frac{\alpha_A}{n_A}\right)^{1/2} + \left(\frac{\alpha_M}{n_M}\right)^{1/2}} \tag{B2}$$

and of Kirkwood (ref. 10) and Muller (ref. 11),

$$E = - \frac{6\mu c^2}{r^6} \frac{\alpha_A\alpha_M}{\frac{\alpha_A}{\chi_A} + \frac{\alpha_M}{\chi_M}} \tag{B3}$$

Equations (B1) to (B3) are of the form

$$E = \frac{C_6}{r^6} \tag{B4}$$

where C_6 is a function of the atomic properties of the constituent atoms. This form is the same as the attractive part of equation (1) with $4\epsilon_{12}(\sigma_{12})^6$ replaced by C_6. Thus, ϵ_{12} was evaluated from each of equations (B1) to (B3) in turn. Calculations of α from equation (4) were then made in every case. Only calculations based on the Kirkwood-Muller formula (eq. (B3)) yielded results in agreement with experimental data (table V). This is consistent with the results of other studies (refs. 19 and 20).

APPENDIX C

SUMMATIONS AND RELATED WORK FOR APPLICATION OF LENNARD-JONES INTERATOM POTENTIAL TO ADSORPTION

An atom is at a distance z above a point P on the $(hk\ell)$ plane of a body-centered cubic crystal of lattice constant a_o. The interatomic distance between this atom and the i^{th} crystal atom is denoted by r_i. It is desired to perform the following two summations for the (100) and (110) crystal planes over the points A, B, and C (fig. 1):

$$S_6[(hk\ell),P,z] = \sum_{i=1}^{\infty} r_i^{-6}\left(\frac{a_o}{2}\right)^6 \tag{C1}$$

$$S_{12}[(hk\ell),P,z] = \sum_{i=1}^{\infty} r_i^{-12}\left(\frac{a_o}{2}\right)^{12} \tag{C2}$$

The origin of z is on the plane passing through the centers of the outermost layer of the crystal atoms, and z is divided into units of $a_o/10$ so that

$$z = \frac{\ell}{10}\, a_o \qquad \ell = 0,1,2, \ldots \tag{C3}$$

$$S_6(100,A,\ell) = 4 \sum_{\substack{p=0,\\ p=\text{even}}}^{\infty} \sum_{\substack{m=1,\\ m=\text{odd}}}^{\infty} \sum_{\substack{n=1,\\ n=\text{odd}}}^{\infty} \lambda_o^{-6} + \sum_{\substack{p=1,\\ p=\text{odd}}}^{\infty} \left[\left(\frac{\ell}{5}+p\right)^{-6} + 4 \sum_{\substack{m=0,\\ m=\text{even}}}^{\infty} \sum_{\substack{n=2\\ n=\text{even}}}^{\infty} \lambda_o^{-6} \right] \tag{C4}$$

$$S_6(100,B,\ell) = \sum_{\substack{p=0,\\ p=\text{even}}}^{\infty} \left[2 \sum_{\substack{n=1,\\ n=\text{odd}}}^{\infty} (\lambda_o^{-6})_{m=0} + 4 \sum_{\substack{m=2,\\ m=\text{even}}}^{\infty} \sum_{\substack{n=1,\\ n=\text{odd}}}^{\infty} \lambda_o^{-6} \right] + \sum_{\substack{p=1,\\ p=\text{odd}}}^{\infty} \left[2 \sum_{\substack{m=1,\\ m=\text{odd}}}^{\infty} (\lambda_o^{-6})_{n=0} + 4 \sum_{\substack{m=1,\\ m=\text{odd}}}^{\infty} \sum_{\substack{n=2,\\ n=\text{even}}}^{\infty} \lambda_o^{-6} \right] \tag{C5}$$

$$S_6(100,C,l) = 4 \sum_{\substack{p=1,\\ p=odd}}^{\infty} \sum_{\substack{m=1,\\ m=odd}}^{\infty} \sum_{\substack{n=1,\\ n=odd}}^{\infty} \lambda_o^{-6} + \sum_{\substack{p=0,\\ p=even}}^{\infty} \left[\left(\frac{l}{5} + p \right)^{-6} + 4 \sum_{\substack{n=0,\\ n=even}}^{\infty} \sum_{\substack{n=2,\\ n=even}}^{\infty} \lambda_o^{-6} \right] \tag{C6}$$

where

$$\lambda_o^2 = \left(\frac{l}{5} + p \right)^2 + m^2 + n^2 \tag{C7}$$

$$S_6(110,A,l) = \sum_{\substack{p=0,\\ p=even}}^{\infty} \left[2 \sum_{\substack{m=1,\\ m=odd}}^{\infty} (\lambda_1^{-6})_{n=0} + 2 \sum_{\substack{n=1,\\ n=odd}}^{\infty} (\lambda_1^{-6})_{m=0} + 4 \sum_{\substack{m=1,\\ (m+n=odd)}}^{\infty} \sum_{n=1,}^{\infty} \lambda_1^{-6} \right]$$

$$+ \sum_{\substack{p=1,\\ p=odd}}^{\infty} \left[(\lambda_1^{-6})_{\substack{m=0\\ n=0}} + 4 \sum_{\substack{m=1,\\ (m+n=even)}}^{\infty} \sum_{n=1,}^{\infty} \lambda_1^{-6} + 2 \sum_{\substack{m=2,\\ m=even}}^{\infty} (\lambda_1^{-6})_{n=0} + 2 \sum_{\substack{n=2,\\ n=even}}^{\infty} (\lambda_1^{-6})_{m=0} \right] \tag{C8}$$

where

$$\lambda_1^2 = 2\left(\frac{\sqrt{2}}{10} l + p \right)^2 + 2m^2 + n^2 \tag{C9}$$

$$S_6(110,B,l) = 2 \sum_{p=0}^{\infty} \sum_{\substack{m=1,\\ m=odd}}^{\infty} \sum_{\substack{n=1,\\ n=odd}}^{\infty} \lambda_2^{-6} \tag{C10}$$

where

$$\lambda_2^2 = 2\left(\frac{\sqrt{2}}{10} l + p \right)^2 + \frac{m^2}{4} + \frac{n^2}{2} \tag{C11}$$

and

$$S_6(110,C,l) = \sum_{\substack{p=0,\\ p=\text{even}}}^{\infty} \left[(\lambda_1^{-6})_{\substack{m=0\\ n=0}} + 4 \sum_{\substack{m=1,\\ (m+n=\text{even})}}^{\infty} \sum_{n=1,}^{\infty} \lambda_1^{-6} + 2 \sum_{\substack{m=2,\\ m=\text{even}}}^{\infty} (\lambda_1^{-6})_{n=0} + 2 \sum_{\substack{n=2,\\ n=\text{even}}}^{\infty} (\lambda_1^{-6})_{m=0} \right] + \sum_{\substack{p=1,\\ p=\text{even}}}^{\infty} \left[4 \sum_{\substack{m=1,\\ (m+n=\text{odd})}}^{\infty} \sum_{n=1,}^{\infty} \lambda_1^{-6} + 2 \sum_{\substack{m=1,\\ m=\text{odd}}}^{\infty} (\lambda_1^{-6})_{n=0} + 2 \sum_{\substack{n=1,\\ n=\text{odd}}}^{\infty} (\lambda_1^{-6})_{m=0} \right] \quad \text{(C12)}$$

The corresponding formulas for S_{12} are obtained by changing the exponents in the sums (C3) to (C12) from 6 to 12. Results of these summations are given in table II (pp. 4 and 5).

The Lennard-Jones 6-12 potential, when applied to adsorption, involves both of these summations in the specific form

$$S_{12\text{-}6}\left[(hkl),P,\frac{2\sigma_{12}}{a_o},l\right] = -\left(\frac{2\sigma_{12}}{a_o}\right)^6 \left\{ \left(\frac{2\sigma_{12}}{a_o}\right)^6 S_{12}[(hkl),P,l)] - S_6[(hkl),P,l] \right\} \quad \text{(C13)}$$

At equilibrium the adsorbed atom is located at l_{min}, which is that value of l for which $S_{12\text{-}6}$ is a minimum. Mathematically l_{min} is defined by

$$\left.\frac{\partial(S_{12\text{-}6})}{\partial l}\right|_{l=l_{min}} = 0 \quad \text{(C14)}$$

and

$$(S_{12\text{-}6})_{min} = S_{12\text{-}6}\left[(hkl),P,\frac{2\sigma_{12}}{a_o},l = l_{min}\right] \quad \text{(C15)}$$

For each value of σ_{12}/a_o there is one corresponding value $l = l_{min}$ for which $S_{12\text{-}6} = (S_{12\text{-}6})_{min}$.

Plots of $(S_{12-6})_{min}$ against σ_{12}/a_o for the six cases of figure 1 (p. 3) are shown in figure 2. The corresponding values are listed in table III (pp. 6 and 7).

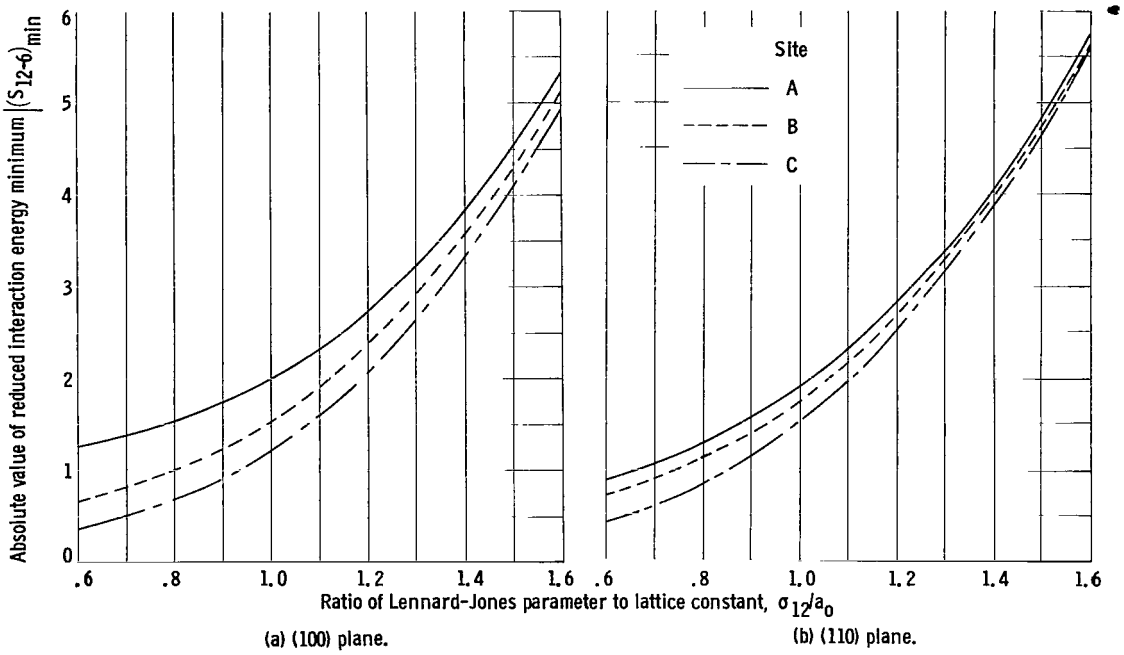

Figure 2. - Reduced interaction energy minimum (eq. (C13)) for body-centered cubic metals as function of reduced Lennard-Jones interatom parameter. (See fig. 1 and appendix C.)

APPENDIX D

COMPARISON OF SUMMATION TECHNIQUE WITH APPROXIMATION METHODS

*Figure 3 compares the results of the following three methods of evaluating $\sum_i \frac{1}{r_i^6}$ for the (110) plane:

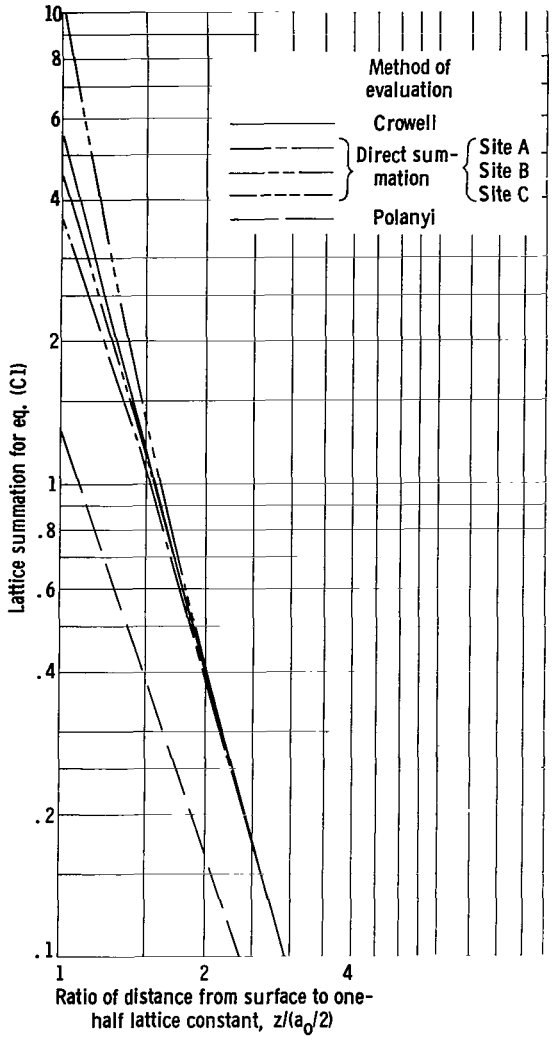

Figure 3. - Three methods of evaluating summation indicated in equation (C1) plotted against reduced distance from surface for plane (110). (See appendix D.)

(1) Polanyi's integral approximation (ref. 21). This method takes the nature of the substrate into account through the inclusion of N, the atomic density; however, it is insensitive to different exposed surfaces and to variations in the adsorbed-particle location.

(2) Crowell's integration-summation method (ref. 22). The crystal lattice is approximated by a set of planes in which the lattice atoms are distributed with uniform density σ. The sum is then replaced by an integration over each plane and a summation of the separate planes. This has the advantage of distinguishing between different exposed surfaces; however, it does not distinguish between different adsorption sites.

(3) The direct summation method (appendix C). This approximation considers the exposed surface and the location of the adsorbed site.

The final expressions for each approximation are as follows:

Polanyi:

$$\sum_i \frac{1}{r_i^6} = \frac{\pi}{6} \frac{N}{R^3} \tag{D1}$$

Crowell:

$$\sum_i \frac{1}{r_i^6} = \frac{\pi}{12} \frac{\sigma}{\varphi^4} \psi^{(3)}(x) \tag{D2}$$

Direct summation:

$$S_6(110,A,l) = \left\{ \sum_{\substack{p=0,\\ p=\text{even}}}^{\infty} \left[2 \sum_{\substack{m=1,\\ m=\text{odd}}}^{\infty} (\lambda_1^{-6})_{n=0} + 2 \sum_{\substack{n=1,\\ n=\text{odd}}}^{\infty} (\lambda_1^{-6})_{m=0} + 4 \sum_{\substack{m=1,\\ (m+n=\text{odd})}}^{\infty} \sum_{n=1}^{\infty} \lambda_1^{-6} \right] \right.$$

$$+ \sum_{\substack{p=1,\\ p=\text{odd}}}^{\infty} \left[(\lambda_1^{-6})_{\substack{m=0\\ n=0}} + 4 \sum_{\substack{m=1,\\ (m+n=\text{even})}}^{\infty} \sum_{n=1}^{\infty} \lambda_1^{-6} + 2 \sum_{\substack{m=2\\ m=\text{even}}}^{\infty} (\lambda_1^{-6})_{n=0} \right.$$

$$\left. \left. + 2 \sum_{\substack{n=2\\ n=\text{even}}}^{\infty} (\lambda_1^{-6})_{m=0} \right] \right\} \qquad \text{(C8)}$$

where σ is the surface density of the substrate atoms, d is the distance between planes in the substrate material, and $\psi^{(3)}(x)$ is the third derivative of the Reimann-Zeta function. Equation (C9) gives λ_1.

Results in figure 3 show that the Polanyi method gives values that are generally too small by about 50 percent. The Crowell approximation is very good, but it lacks ability to distinguish between different adsorption sites on the substrate surface.

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